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Water-Based Halon Replacement Sprays

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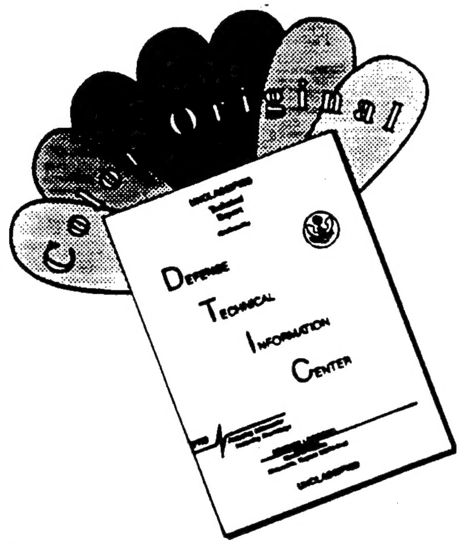

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13. ABSTRACT *(Maximum 200 words)*

Water delivered as a spray is more effective against hydrocarbon fires than a stream of water. Water as a mist is even more effective. The delivery system influences the effectiveness of water. The major problem with using water in a combat vehicle is freezing at low temperatures. Additives can be added to lower the freezing point. Thus, water solutions may be usable under all expected operating conditions. Experiments have been conducted using sprays of water and water with additives to extinguish JP-8 pool fires. Additives were chosen to provide low freezing points to the water and to improve the fire-extinguishing capability of the water. As expected, sprays of just water were not particularly effective for extinguishing JP-8 pool fires. Water with calcium chloride, added to give a −55° C freezing point, showed no improvement in fire suppression over the baseline water tests. Other additives, however, showed remarkable improvements over the water case.

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1. INTRODUCTION

The U.S. Army has been involved in the search for a replacement for Halon 1301 ever since halons were identified as ozone-depleting agents in the Montreal Protocol of 1987. Halon 1301 is currently used in Army combat vehicles to suppress hydrocarbon fires in both crew and engine compartments. Several agents (perfluorocarbons) have been identified as nonozone depleting and of very low toxicity. However, other environmental concerns have been raised, such as the agents' potential contribution to global warming. While any global warming potential has not been accurately defined, there is a hesitancy to pick a halon replacement agent that may eventually be classed in an environmentally unacceptable group. This would require a new search for a replacement agent. A halon replacement with no environmental problems is desired. An attractive candidate for this role is water.

It has been found that water is not really very effective in extinguishing a hydrocarbon fire unless that water is delivered to the fire in the form of a mist (very small droplets). Large droplets of water are far less effective, and water in the form of a stream is still less effective. The principal problem with very small droplets of water is that they do not penetrate through the air easily. Large droplets have less air resistance than small droplets; hence, the large droplets travel more easily through air. But the large droplets can pass through a flame with little evaporation since their surface-to-volume ratio is small. The smaller mist droplets with larger surface-to-volume ratios can evaporate easily in a flame, making them more efficient than the large droplets.

The approach reported in this paper is to add materials to water, which can increase the efficiency of the large spray droplets. These large water-based droplets might approach the efficiency of the small mist droplets in extinguishing flame, while retaining the ability to penetrate air more easily than mist droplets. The addition of certain salts to water might also solve the problem of the water freezing in vehicles during cold weather.

2. EXPERIMENTAL

2.1 Fuel. The fuel used in this study was JP-8, which the Army has chosen as the single fuel for use on the battlefield. This fuel has a flashpoint above room temperature, typically about 50° C (122° F). The JP-8 used in this work had a flashpoint of 55° C (130° F).

2.2 Spray Device. A commercial airless paint sprayer was used to spray droplets of water-based agents onto fuel fires. Tests showed that the device sprayed water at the rate of 4.2 g/s. Droplets of spray were collected and analyzed for particle size using an optical microscope.

2.3 Setup. The setup used in these fire-extinguishing experiments consisted of a pan, 14 cm in diameter × 6.3 cm high, into which 700 ml of JP-8 fuel was poured. The fuel surface was approximately 2.5 cm below the top of the container. Two strands of absorbent paper (wicks) were placed over the rim of the pan, dipping into the fuel.

The spray nozzle was placed 46 cm from the center of the fuel container, elevated 23 cm higher than the rim of the container. The nozzle was aimed at a point 2.5 cm above the top of the container, depressed 26.5° from the horizontal. Tests showed that, when the sprayer was activated, water was collected in the pan at the rate of 1.35–1.50 g/s. A photograph of the setup is given in Figure 1.

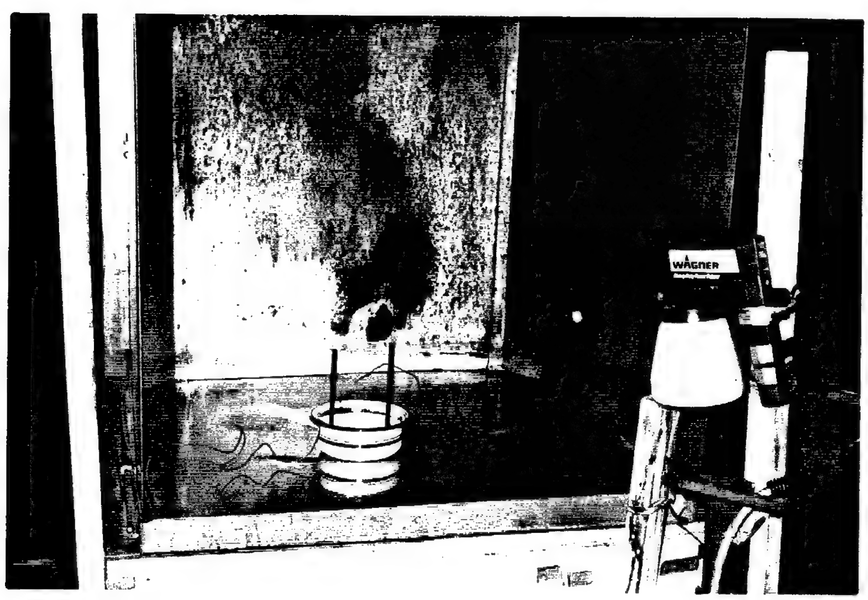

Figure 1. Test setup.

3. RESULTS AND DISCUSSIONS

3.1 Fire-Out Times. Table 1 gives the fire-out times for sprays of water and 12 water-based solutions. Data are presented for agents at three temperatures: 5° C, 22° C, and 77° C. Each fire-out time in the table is an average of two to four tests. The sums of the fire-out times at the three temperatures are added to give an overall ranking, the lowest time being best. The physical state of the agents at −18° C is also given. This is the lowest temperature available using a conventional laboratory freezer.

Table 1. Rankings of Fire-Extinguishing Sprays

Rank	Agent	Time (5° C) (s)	Time (23° C) (s)	Time (77° C) (s)	Total Time (s)	State at −18° C
1	60% K lactate	0.3	2.4	0.5	3.2	liquid
2	60% K acetate	1.8	1.0	0.5	3.3	frozen
3	10% Na Br	2.4	0.7	3.1	6.2	frozen
4	8% K Br in 29% $CaCl_2$	5.1	4.6	2.7	12.4	liquid
5	29% CaI_2	7.6	3.4	5.4	16.4	frozen
6	10% K Br	6.2	6.8	3.4	16.6	frozen
7	12% Pyrocap in 29% $CaCl_2$	7.0	4.9	5.1	17.0	thick liquid
8	10% NH_4I	5.2	5.7	9.4	20.3	frozen
9	12% Na Br in 29% $CaCl_2$	5.3	14.4	5.0	24.7	liquid
10	water	15.5	9.0	7.4	31.9	frozen
11	10% ammonium citrate	8.4	9.3	17.4	35.1	frozen
12	10% NH_4 Br	10.3	6.0	21.4	37.7	frozen
13	29% $CaCl_2$	16.0	6.5	20.2	42.7	liquid

3.2 Size of Droplets. Spray droplets were collected and examined under an optical microscope. Initially, water droplets from the airless sprayer were collected. It was found that these droplets

evaporated quickly due to the heat from the high-intensity lamp of the microscope. Therefore, droplets of a 60% potassium lactate in water solution were collected on a greased microscope slide and photographed in the optical microscope.

It was found that the droplets from the airless spray were smaller than expected. The maximum of the particle number vs. size distribution was in the 50–100 μm diameter range. Approximately 95% of the droplets were 200 μm diameter or smaller. No droplets over 400 μm diameter were found.

3.3 Comparison of Water-Based Sprays. Figures 2–5 present, in graphical form, comparisons of the 12 water-based solutions with water as the baseline. It can be easily seen that, while some of the solutions are significantly more effective than water, other solutions are less effective than water. All solutions were tested for fire-extinguishing effectiveness at liquid temperatures of 5° C, 23° C, and 77° C. This gave an indication of the effectiveness of the spray materials over a range of expected vehicle temperatures.

3.4 Comparison of Sprays Which Were Liquids at −18° C. The five agents that were liquid at −18° C are compared to water and each other in Figures 6 and 7. It can be seen that the 60% potassium lactate in water solution is the best performing of the solutions that have low-temperature possibilities. It should be mentioned that the 60% potassium lactate in water solution had a freezing point of −63° C, measured by the Chemistry Lab at the U.S. Army Aberdeen Test Center. One low-temperature agent, a 40% solution of potassium carbonate in water, was rejected from consideration due to its excessively caustic nature. Its pH was measured as 12.9. A pH above 12 identifies a material as hazardous waste requiring special treatment in cleanup and disposal.

3.5 Comparison of Individual Ions. Figure 8 gives the comparison of two solutions, the first, a 29% by weight calcium chloride in water solution, and the second, a 29% by weight calcium iodide in water solution. The iodide solution is significantly better as a fire-extinguishing agent at all three temperatures. The nature of the anion does have an effect on the fire-extinguishing ability of the salt solution. The iodide is more effective than the chloride, on an equal weight of salt basis, at all three temperatures.

Figure 9 gives the comparison of a 10% by weight ammonium bromide in water solution vs. a 10% by weight ammonium iodide in water solution. The two solutions are approximately equivalent at 5° C and 23° C. It is only at 77° C that the ammonium bromide is inferior as an extinguishing agent. It would

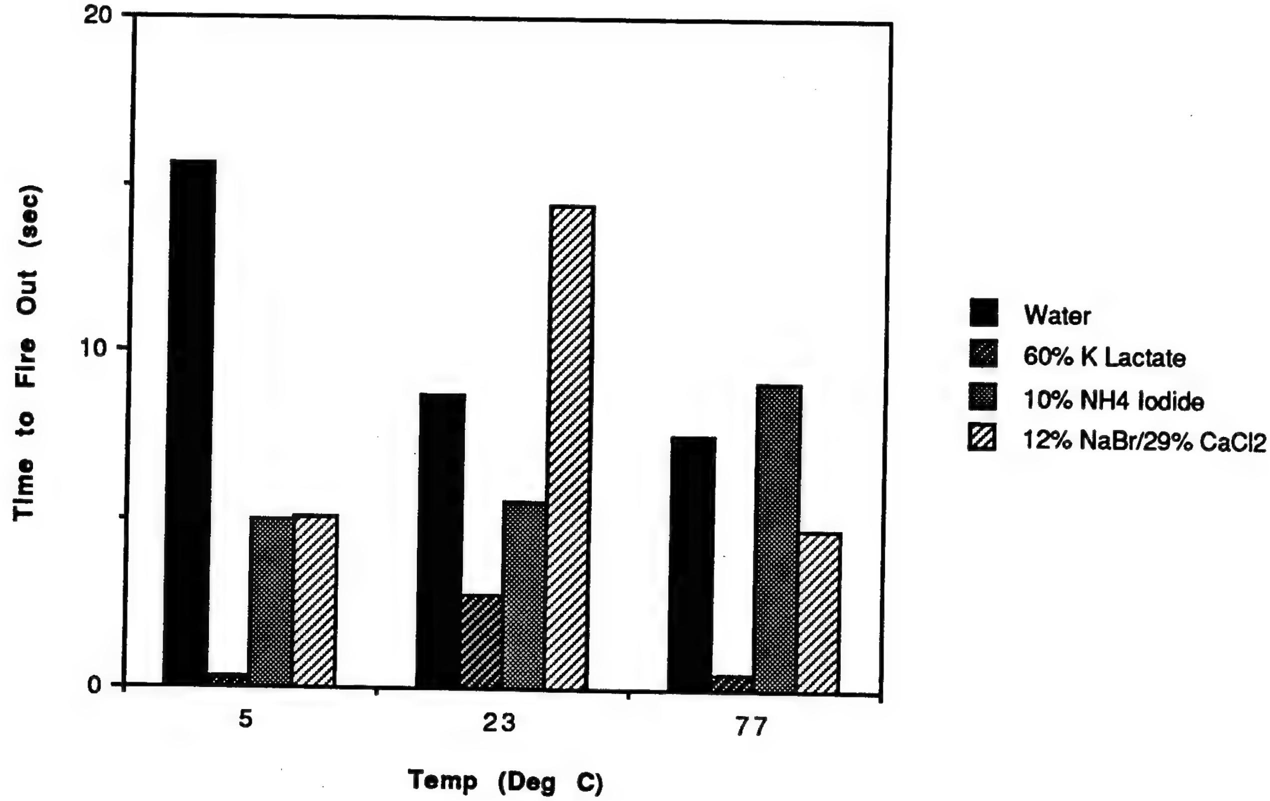

Figure 2. Water and various agents vs. JP-8 flame I.

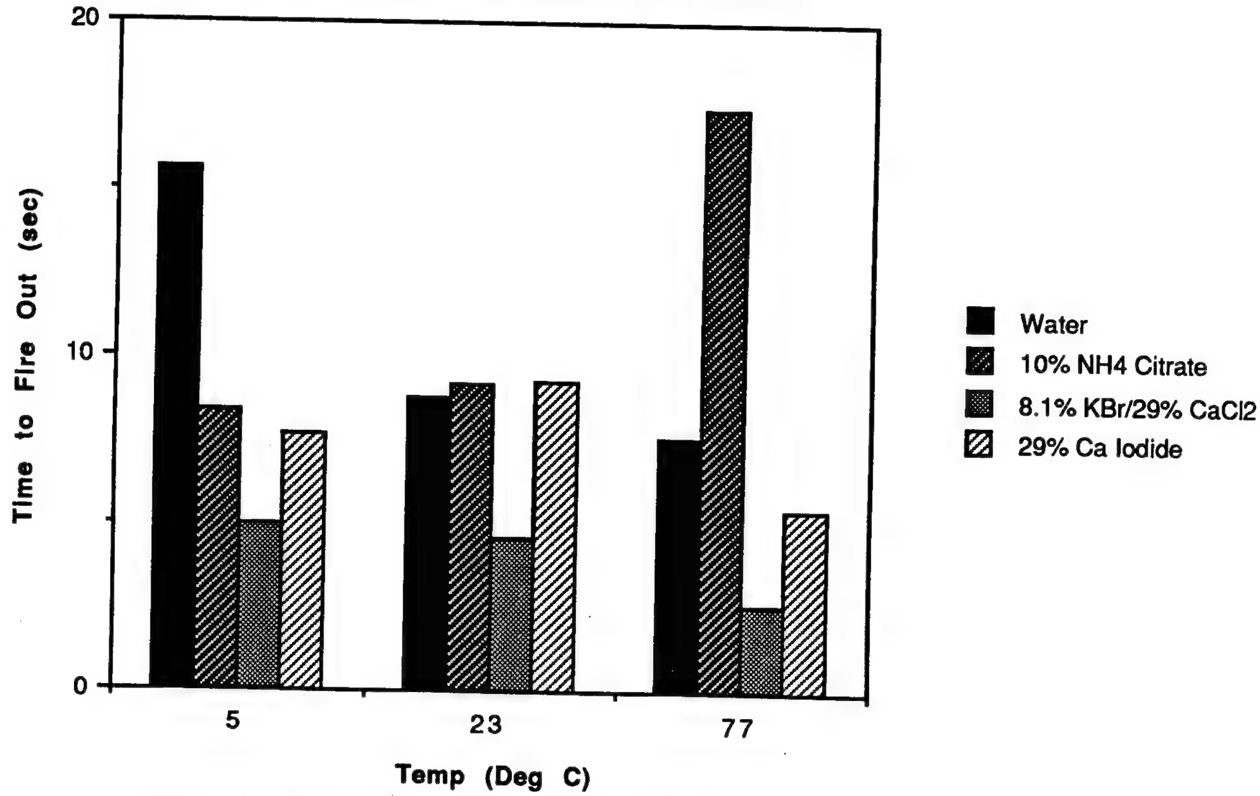

Figure 3. Water and various agents vs. JP-8 flame II.

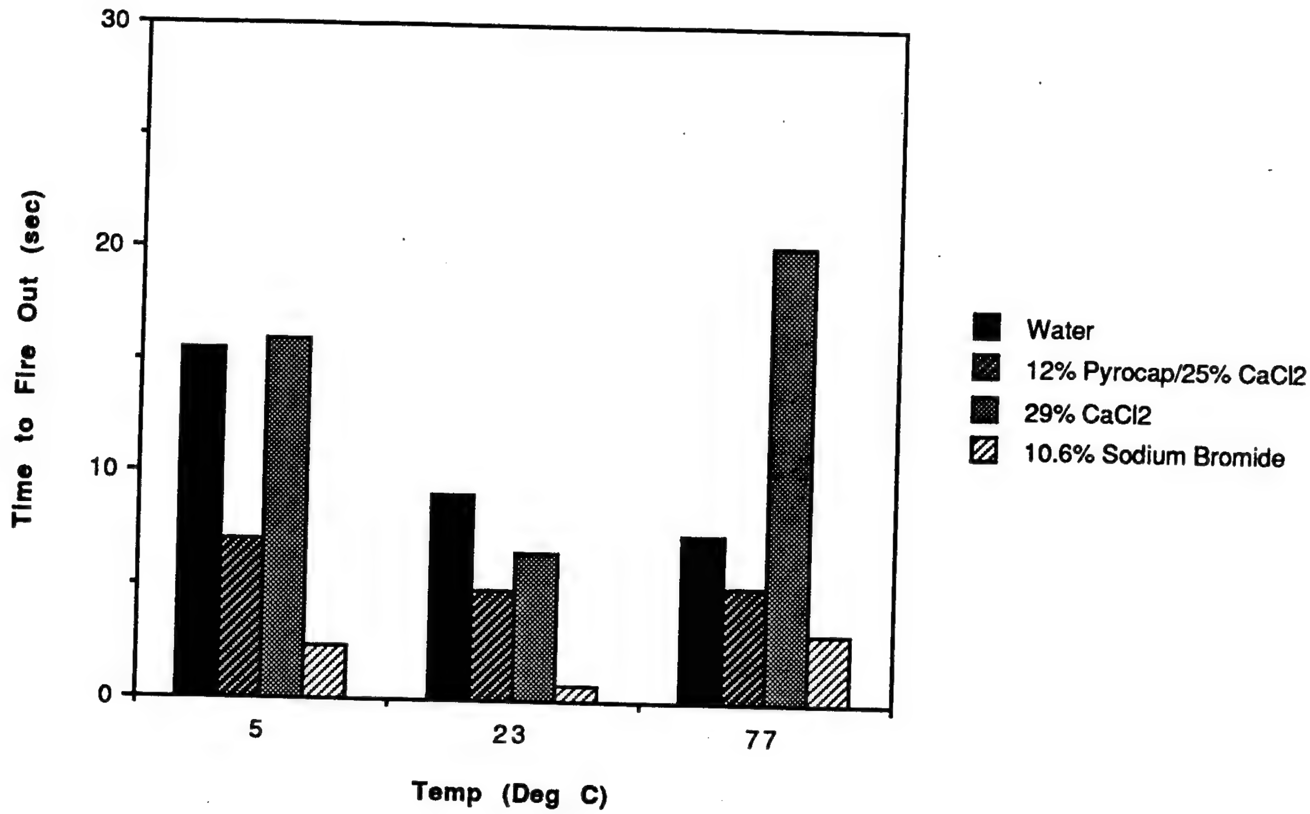

Figure 4. Water and various agents vs. JP-8 flame III.

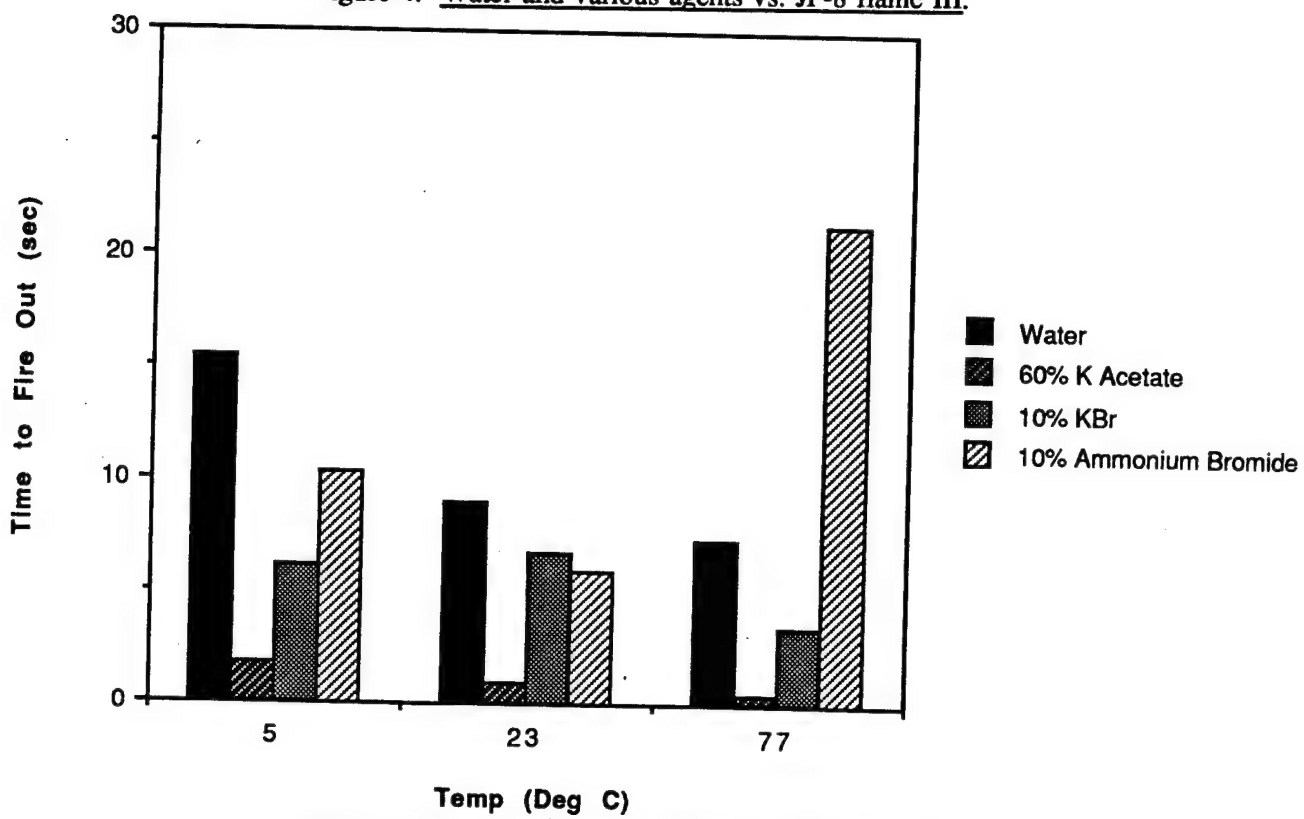

Figure 5. Water and various agents vs. JP-8 flame IV.

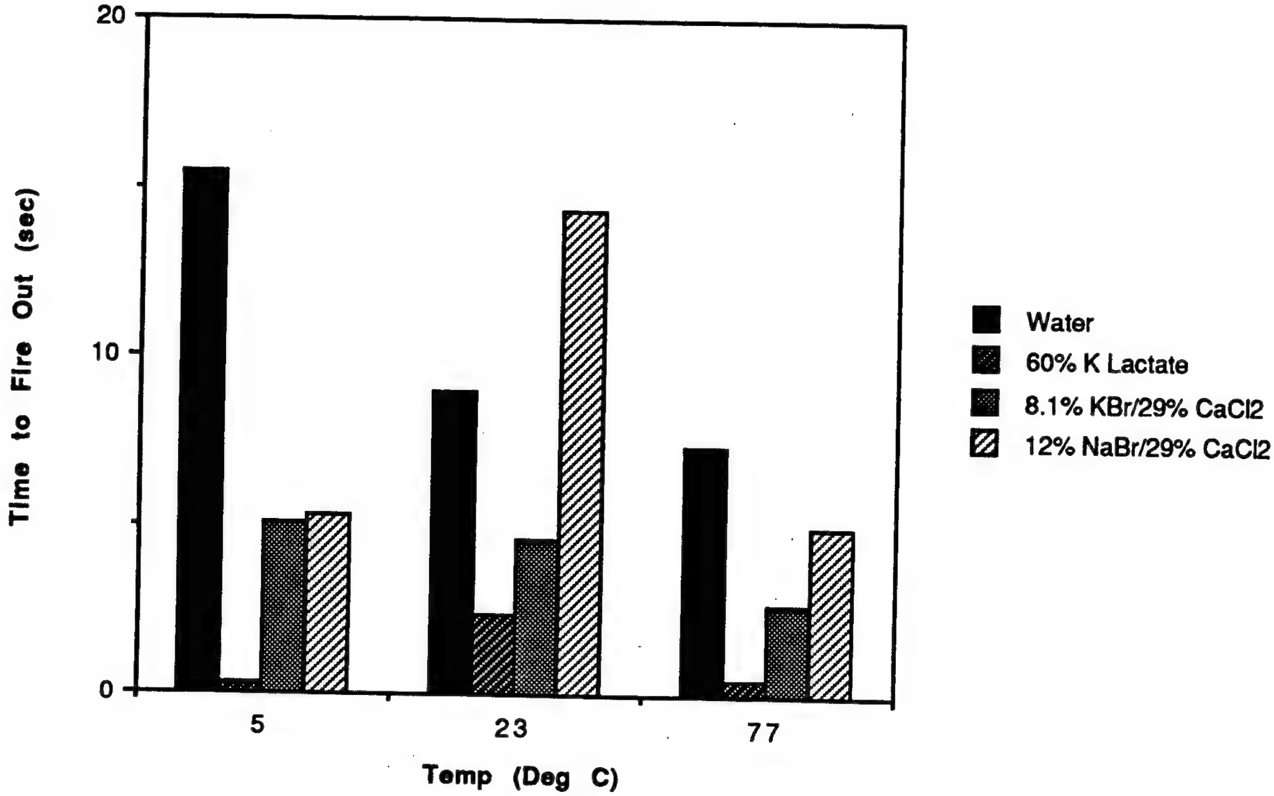

Figure 6. Water and low-temperature agents vs. JP-8 flame I.

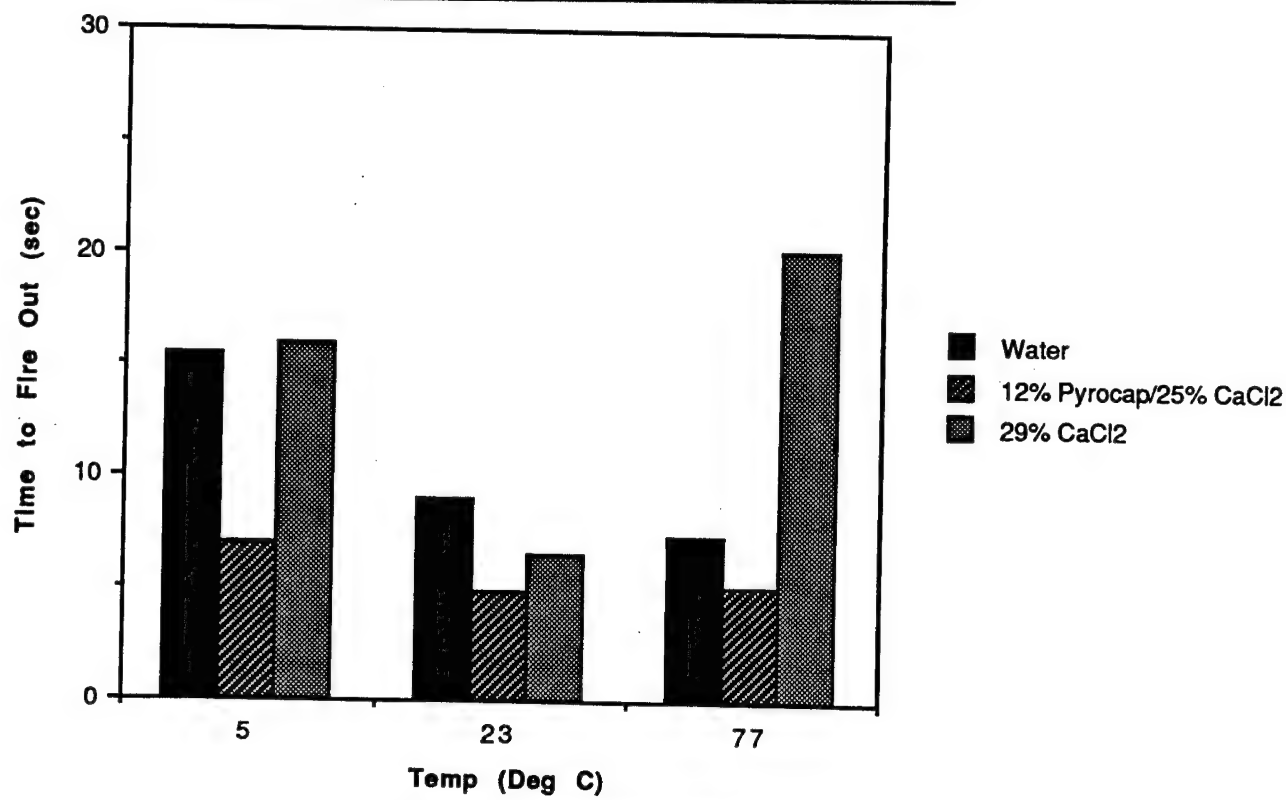

Figure 7. Water and low-temperature agents vs. JP-8 flame II.

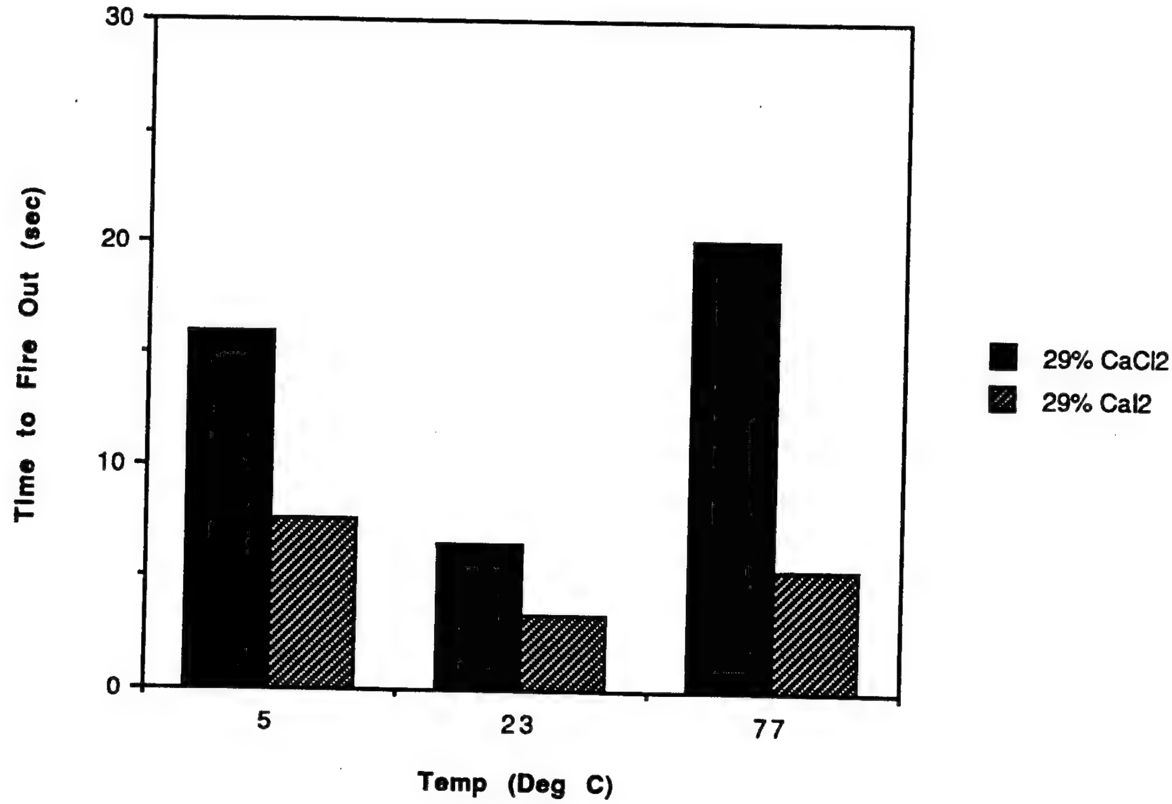

Figure 8. 29% calcium chloride vs. 29% calcium iodide.

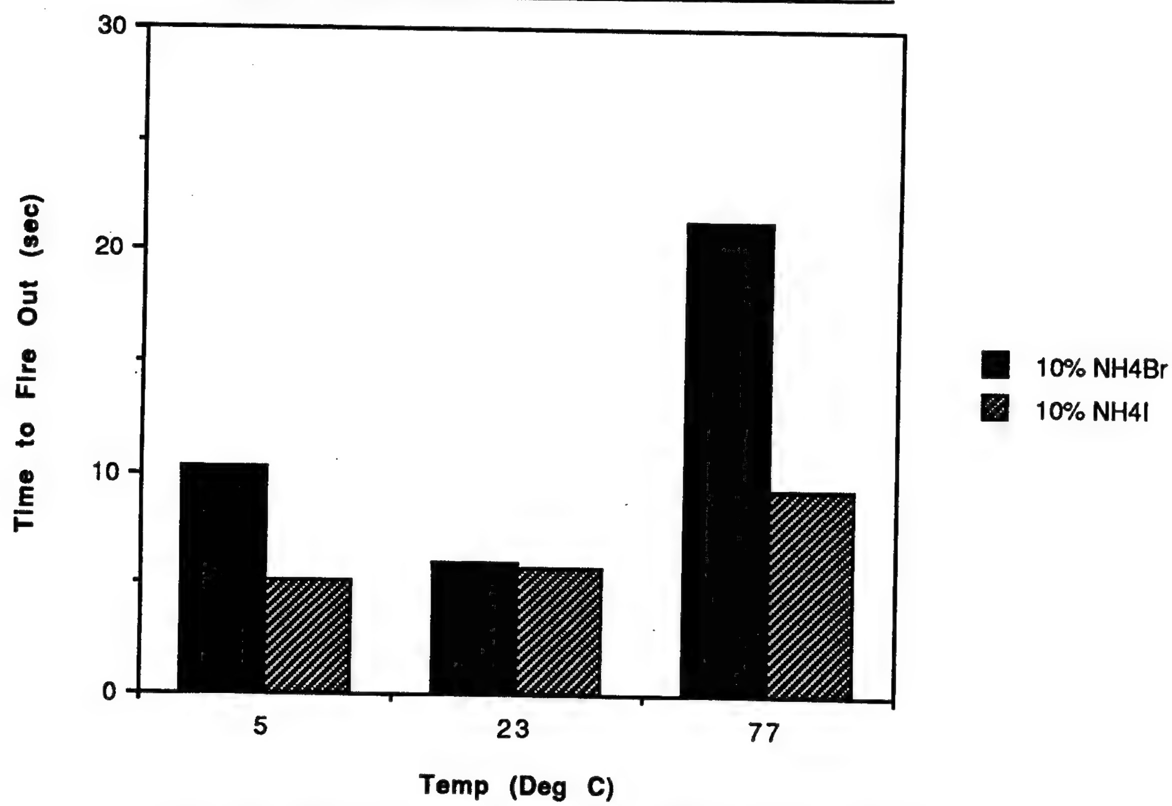

Figure 9. 10% ammonium bromide vs. 10% ammonium iodide.

be expected that the bromide anion and the iodide anion would be approximately equivalent in their ability to extinguish fires. The poor performance of ammonium bromide at 77° C was unexpected.

Figure 10, a comparison of 10% by weight solutions of ammonium bromide in water and sodium bromide in water, shows that the sodium cation is much more effective than the ammonium cation, in extinguishing fire, on an equal weight of salt basis. It is also apparent, from the figure, that sodium bromide also loses some of its effectiveness at 77° C, compared to 5° C and 23° C.

Figure 11 shows the comparison of 10% by weight in water solutions of sodium bromide vs. potassium bromide. The sodium cation was found to be more effective than the potassium cation on an equal weight of salt basis. While potassium salts are reported to be more effective than sodium salts as extinguishing agents (Allman et al. 1983), those comparisons are on a molar basis, not on a weight basis.

4. MECHANISM

Possible mechanisms by which the water-based sprays extinguished the fuel fires include the following.

4.1 Lowering Flame Temperature. There is a cooling effect, in which droplets enter the flame zone and evaporate. This cooling lowers the flame temperatures and can lead to extinction of the flame. This scenario is shown in Figure 12. The flame of a hydrocarbon will be extinguished when the flame temperature falls to approximately 1,600° C (Lewis and von Elbe 1961).

4.2 Lowering Liquid Temperature. There can be a cooling effect, in which droplets fall into the liquid fuel and lower the fuel temperature. This lowers the rate of fuel evaporation. When the liquid is cooled below its firepoint, the flame will be extinguished. Figure 13 shows this situation. For this mechanism to be viable, it is necessary for the firepoint of the liquid fuel to be a higher temperature than the temperature of the droplets. Thus, the droplets can have a cooling effect on the liquid sufficient to cause extinguishment. Typically, with liquid hydrocarbon fuels, the firepoints are only a few degrees above the flashpoints. Thus, for the JP-8 fuel used in this study, with a measured flash point of 55° C, the firepoint should be 60° C, maximum. This mechanism can be important for the tests where the agents were at 5° C and 23° C. For the tests with hot agents, 77° C, this mechanism would not be important.

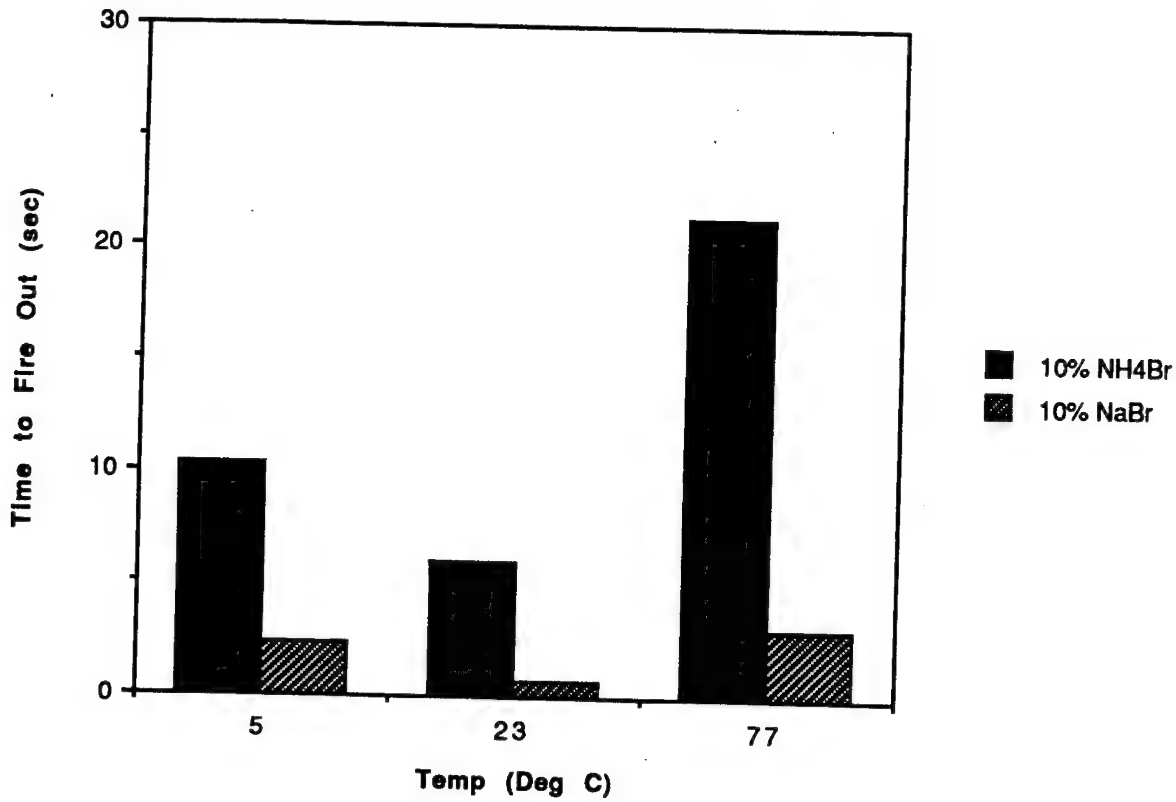

Figure 10. 10% ammonium bromide vs. 10% sodium bromide.

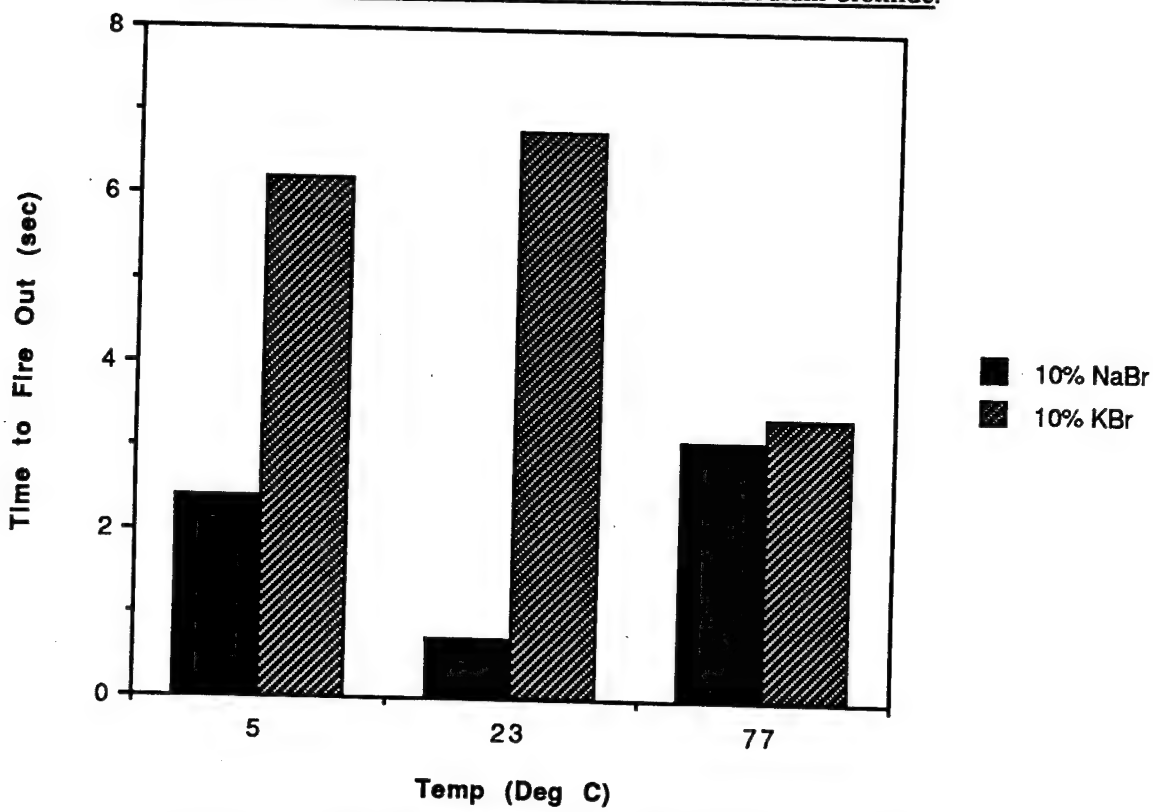

Figure 11. 10% sodium bromide vs. 10% potassium bromide.

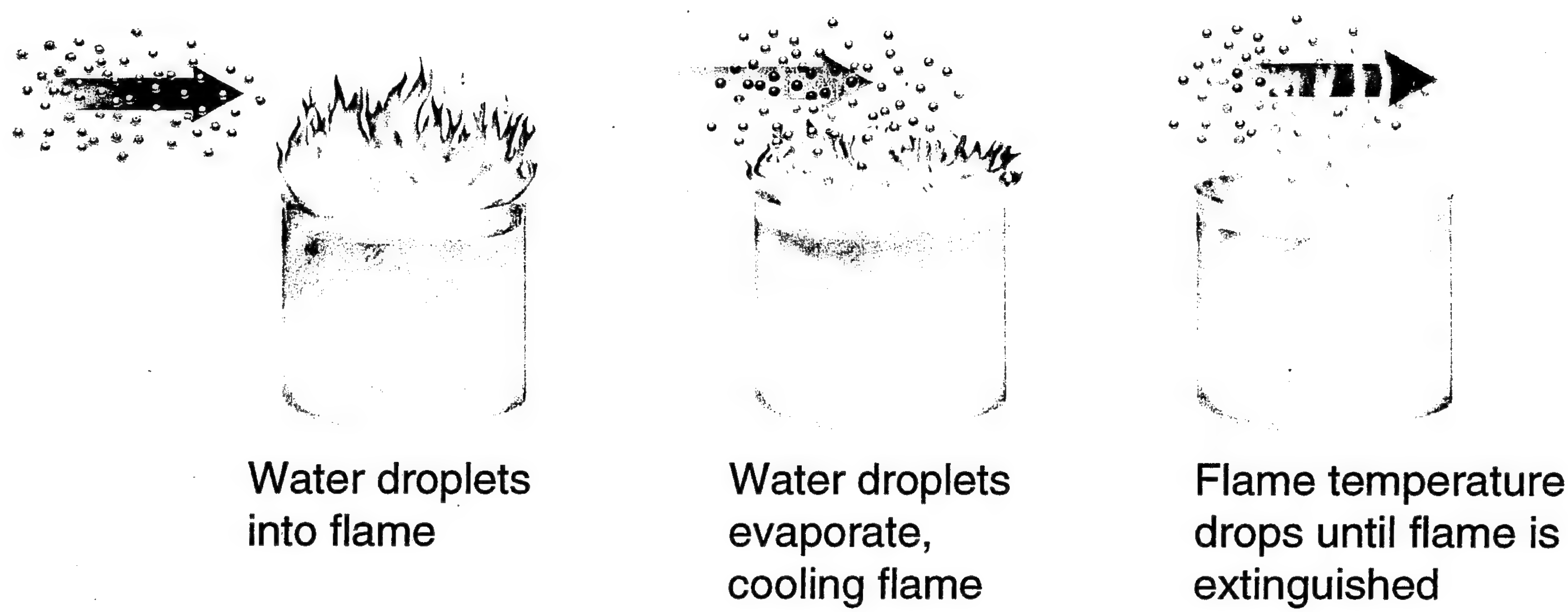

Figure 12. Mechanism I - Droplets evaporate cooling flame.

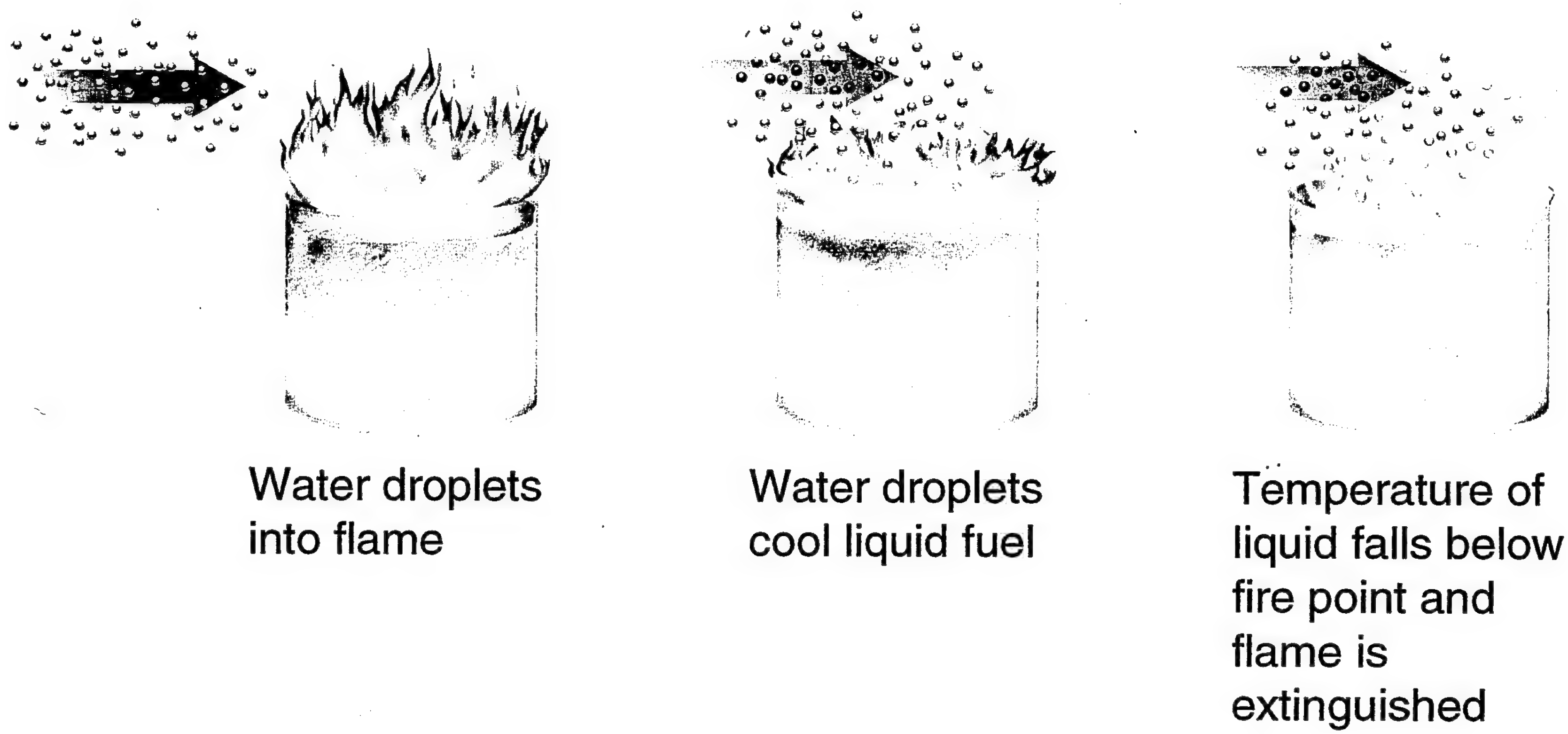

Figure 13. Mechanism II - Droplets cool liquid fuel.

4.3 Steam Dilutes Air. When a water-bearing droplet enters the flame, there will be at least some evaporation of the liquid water. If the water droplets are with the air that is needed for combustion, the water vapor dilutes all components of the air, including the oxygen. This is shown in Figure 14. A fall in oxygen partial pressure will lower the rate of combustion. In a hexane-air system, diluted with steam (Coward and Jones 1952), all mixtures with less than 13.5% oxygen are nonflammable.

4.4 Quenching by Solid Particles. When droplets of a solution of a salt in water are heated by the flame, water can evaporate, leaving solid particles of the salt. This is depicted in Figure 15. Particles of any noncombustible solid can be used to quench flames. However, some solids are much more efficient than others. Powders, such as purple K (potassium bicarbonate with a purple dye for identification), sodium bicarbonate, and Super K (potassium chloride) are common fire-extinguishing agents. In general, it has been found that potassium salts are more effective than sodium salts. The use of sprays containing dissolved salts that are effective fire-extinguishing agents allows one to direct a powder into the flame of a hydrocarbon fire without filling an entire enclosure with powder. The powder forms due to evaporation of water from the droplets, only where the powder is needed—in the flame zone. It is also possible to dissolve a salt that has the ability to lower the freezing point of water, forming an all-weather agent.

4.5 Blowoff. Figure 16 shows the case in which liquid droplets and entrained air are directed to the flame. The airstream can lift the flame off the liquid surface and off anything that may be acting as a flame holder (rim of the container for the liquid fuel). The lifted-off flame will have a decreased heat feedback to the fuel. As the temperature of the fuel falls, the rate of fuel evaporation decreases. This leads to flame extinction.

4.6 Application of Mechanisms to Specific Agents. In actuality, more than one of these mechanisms will be operational in most cases of using sprays to extinguish a hydrocarbon fire. In some cases, one of the mechanisms may be much more important than any of the others; in other cases, a combination of mechanisms may be responsible for extinguishing fires.

In the case of a water spray, it was observed that the spray caused lift-off of the flame from both the liquid fuel surface and the rim of the pan. There were also liquid water droplets which struck the fuel surface. The temperature of the fuel decreased until the flame was extinguished. At a water temperature of 5° C, the fire-out time was 15.5 s. At a water temperature of 23° C, the fire-out time was less, 9.0 s. This indicates another phenomenon; most likely evaporation of the water droplets in the flame was

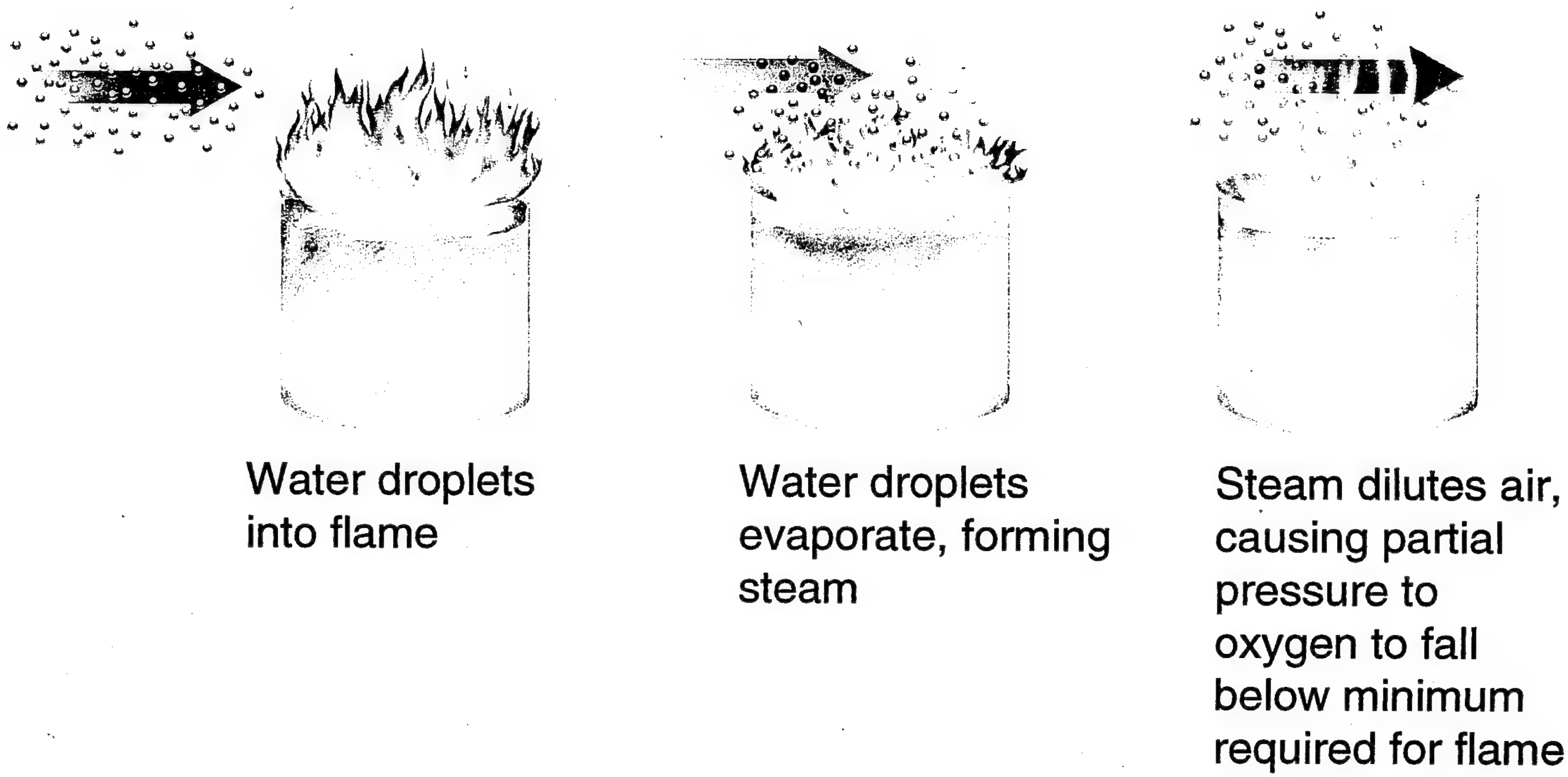

Figure 14. Mechanism III - Droplets evaporate forming steam.

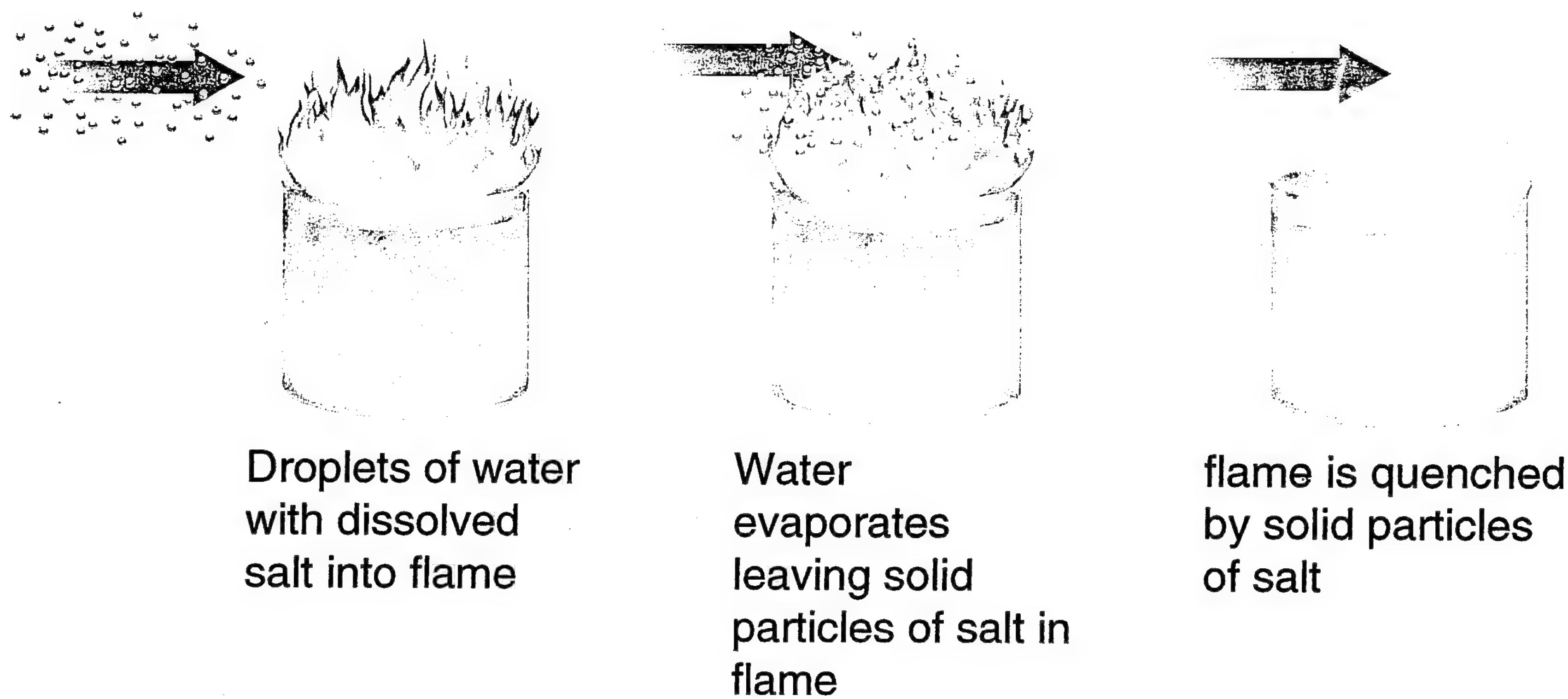

Figure 15. Mechanism IV - Water evaporates forming solid particles.

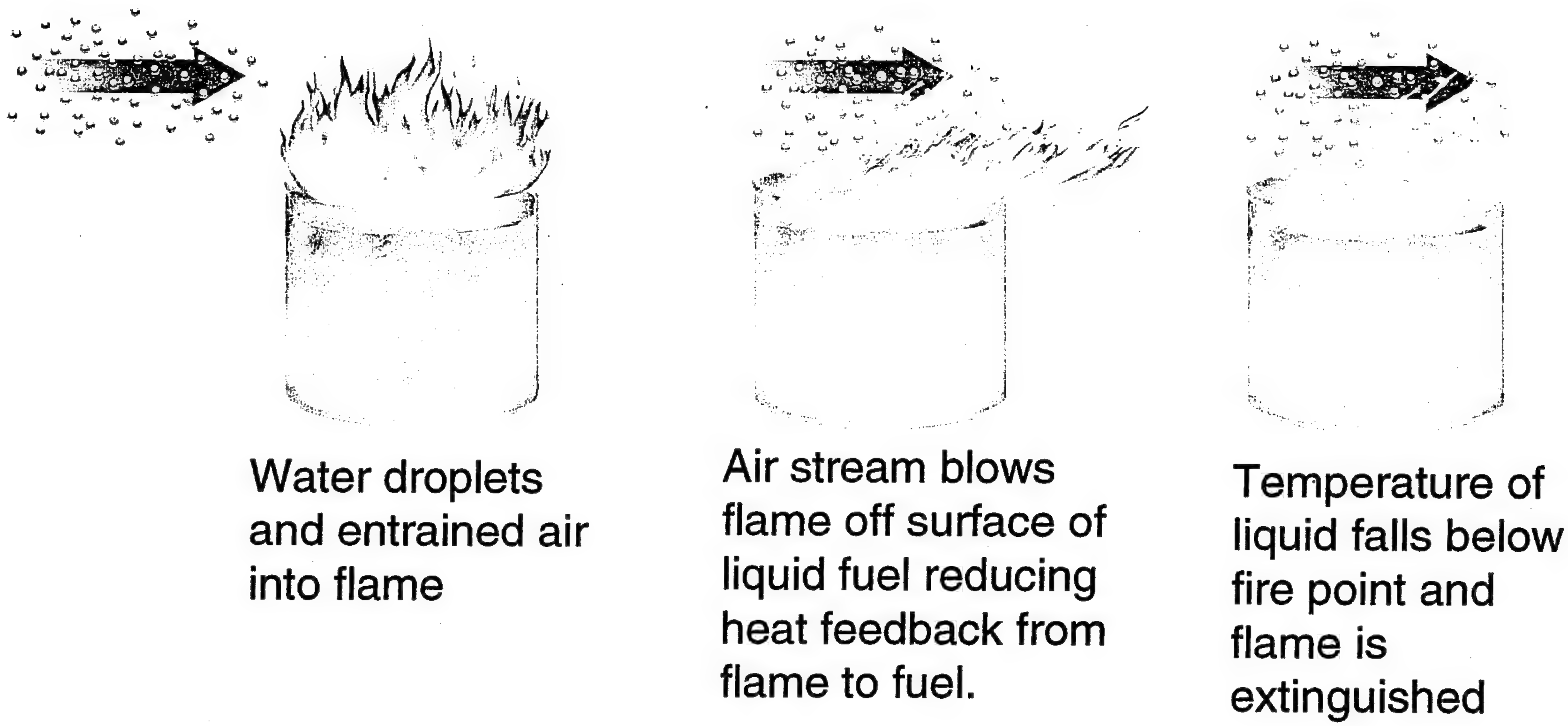

Figure 16. Mechanism V - Flame blown off surface of fuel.

greater at 23° C, cooling the flame and causing even less heat feedback to the liquid fuel. At 77° C, the fire-out time with water was 7.4 s, indicating even more evaporation of water droplets in the flame and an even cooler flame. The decrease in the partial pressure of oxygen due to steam formation will also lower the rate of combustion and heat generation. This contributes to cooling of the fuel by lowering the heat feedback mechanism.

In the case of the 29% calcium chloride in water solution, the fire-out time at an agent temperature of 5° C was 16.0 s, indicating the flame blowoff and droplets impinging the fuel surface was responsible for flame extinction, just as for water at 5° C. At 23° C, the fire-out time was 6.5 s, quite similar to water at the same temperature. An increase in the evaporation of water from the droplets may be responsible for a lower fire-out time than was found at 5° C. At 77° C, the fire-out time is quite long, 20.2 s. A possible explanation is that the water droplets evaporated quickly when they entered the heated leading edge of the flame. There was less water per droplet, since the droplets are only 71% water. Therefore, there was less cooling of the flame. Any solid calcium chloride that formed would not be an effective fire-extinguishing salt. Therefore, the 29% calcium chloride solution was less effective than neat water as a fire-extinguishing spray, at least at high-agent temperature.

Using a 10% ammonium iodide spray, the fire-out times are reasonably identical at the three agent temperatures, between 5.2 s at low temperatures to 9.4 s at the high temperature. Some of the water droplets are evaporating even at the low temperature. The ammonium iodide salt has an effective solid surface for flame quenching.

In the case of the 29% calcium iodide in water solution, the fire-out times were uniformly low. There was evaporation of water from some droplets in the flame. The calcium iodide is effective as a flame-quenching salt.

The final examples are the 60% by weight solutions of potassium lactate and potassium acetate in water. Each solution was found to be extremely effective in extinguishing the pan fires. The flames were extinguished as soon as the spray arrived at the pan fire. The water evaporated quickly since the droplets were only 40% water. The potassium lactate and potassium acetate solids were extremely effective as solid fire extinguishers. The sprays of these materials provided a convenient method of putting powder fire extinguishing agents into flames without having an excess of powder. The powder formed from the evaporation of water, only where required, in the flame.

5. CONCLUSIONS

(1) Two of the sprays tested, a solution of 60% potassium lactate in water and a solution of 60% potassium acetate in water, were far superior to the other sprays for extinguishing JP-8 pan fires. It is believed that the high salt content of these solutions is important. The evaporation of the 40% water can occur quickly once the spray droplets encounter a flame. The solid salts released are excellent fire-extinguishing agents. The solids form only in the flame zone, where they are needed. Thus, there is no excess of fire-extinguishing powder. The powder particles are formed only where they can quench the flames.

(2) All of the sprays, at 23° C and 5° C, had the ability to extinguish JP-8 pan fires. Some of the sprays extinguished simply by cooling the liquid fuel to a temperature below the fire point. These sprays did not have the ability to extinguish by interacting with the flames.

(3) Sprays of solutions containing iodide salts were superior to sprays of bromide salt solutions, when used to extinguish JP-8 pan fires.

(4) Solutions of both sodium and potassium salts exhibited good fire-extinguishing ability when used as sprays against the pan fires.

(5) Salts containing chloride anions did not enhance the fire-extinguishing ability of the sprays. In fact, a 29% calcium chloride in water spray was a poorer fire-extinguishing agent than neat water.

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